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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : **A01N 25/34, 65/00, 37/18 // (A01N 65/00, 25:34) (A01N 37/18, 25:34)**	**A1**	**(11) International Publication Number:** **WO 99/09824** **(43) International Publication Date:** 4 March 1999 (04.03.99)

(21) International Application Number: PCT/US98/17371

(22) International Filing Date: 19 August 1998 (19.08.9

(30) Priority Data:
60/056,843 22 August 1997 (22.08.97) US

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(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PESTICIDAL PACKAGING MATERIALS

(57) Abstract

A pesticide is disposed in or on a packaging material to provide a composite article that protects products packaged therein from pest such as fungi and insects. The pesticide includes an essential oil or at least one pesticidally active component of thereof. The packaging material can be flexible or substantially rigid and can be thermoplastic or non-thermoplastic.

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PESTICIDAL PACKAGING MATERIALS

BACKGROUND INFORMATION

1. Field of the Invention

This invention relates to packaging materials, particularly those materials used to package products susceptible to pests such as insects, fungi, and the like

2. Background of the Invention

Throughout history, pests have circumvented mankind's efforts to store sensitive products for extended periods of time. Despite repeated efforts to develop methods for eliminating pests from packaged goods, the problem still remains. Huge amounts of food products are lost each year due to infestation by insects and spoilage due to fungi

Additionally, some methods of eliminating pests from packaged goods are being reexamined in view of environmental concerns. For example, a popular method to eradicate insects from grain storage areas is fumigation with a toxic gas such as methyl bromide; however, this technique is under increasing criticism by environmental groups and review by governmental agencies. Additionally, such fumigation techniques do nothing to prevent infestation after the product is packaged

To make the problem even more intractable, many very effective pesticides (e.g., those pesticides that contain halogen atoms) cannot be used in contact with food because of toxicity concerns. Therefore, when one wishes to package food products for storage or retail display, the number of useful pesticides dwindle significantly. Additionally, those that are available often are effective against only a very limited number of pests. For example, although a particular pesticide repels and/or kills certain types of moths, it might exhibit limited or negligible effect with respect to other types of moths

For centuries, essential oils derived from a variety of plants, including the neem tree, have been a source of compounds used as medicines, therapeutics and, of interest for present purposes, insecticides. Despite repeated exposures, insects apparently have not developed a resistance to many such oil-derived compounds. This continued efficacy has drawn the attention of many who continue to search for natural insecticides. Various components of such oils have been shown to both kill and repel insects as well as controlling the growth of fungi. Many of these components have been proposed to be included in standard pesticidal formulations such as, for example, dispersions, powders, pastes, granules, aerosols, candles, and the like.

Provision of packaging materials with the capability to repel and/or kill pests to a degree such as that exhibited by neem seed components continues to be highly desirable within the packaging and food processing industries.

SUMMARY OF THE INVENTION

Briefly, the present invention provides a composite article that includes a packaging material and an effective amount of a pesticide disposed on or incorporated in the packaging material. The pesticide includes an essential oil or at least one pesticidally active component of neem oil and/or a standard pesticide such as N,N-diethyl-*m*-toluamide (DEET).

In another aspect, the present invention provides a package that includes a product surrounded by the foregoing composite article.

In yet another aspect, the present invention provides a method of protecting a product from one or more pests. In this method, the product is surrounded by the above-described composite article so as to form a package. The composite article provides protection against pests to the product.

In a still further aspect, the present invention provides a method of making a protective film. In this method, an essential oil or a pesticidally active component thereof and/or a pesticide such as DEET is blended with one or more polymers which are then extruded so as to form the film. Depending on the end use for the film, it can be processed in any of a variety of ways (e.g., oriented, cast, blown, annealed, etc.) so as to provide desired physical characteristics.

The composite article of the present invention can take many forms. Non-limiting examples include impregnated paper or paperboard, coated paper or paperboard, impregnated films, coated thermosetting materials or films, and the like. Depending on the particular form which the composite article of the present invention takes, it can be used as a primary or secondary packaging material.

Because many types of retail and wholesale goods are subject to destruction or infestation by a variety of pests, the scope of goods for which the composite article of the present invention can provide protection is quite large. Categories of such goods include, but are not limited to, textiles, paper, books, building materials (particularly wood), clothing such as woolen articles, fish meal, and foods. Among the last category, non-limiting examples include processed and unprocessed grains, rice, dry mixes, fresh and dried fruits, vegetables, dairy products, coffee and cocoa beans, processed chocolate, seeds, pet foods, and the like.

Regardless of form, the composite article of the present invention has the advantage of being able to repel and/or kill a wide variety of pests. Types of fungi against which certain essential oils, including neem oil and certain neem oil-derived compounds, have shown fungicidal activity include mildews, rusts, dollar spots, brown patch, black spots, botrytis, and the like. Types of insects against which the same and other essential oils, including neem oil and certain neem oil-derived compounds, have shown insecticidal activity include Indian meal moths, mealy bugs, mites, fleas, roaches, weevils, aphids, as well as certain beetles and flies. Advantageously, many essential oils, including neem oil, are not known to harm such beneficial insects as bees.

To assist in understanding the more detailed description of the invention that follows, certain definitions are provided immediately below. These definitions apply hereinthroughout unless a contrary intention is explicitly indicated:

"insecticide" means a compound or composition with the ability to kill or repel insects and/or their larvae, ova, etc.;

"fungicide" means a compound or composition with the ability to kill or inhibit growth of fungi;

"pest" means an insect or fungus;

"pesticide" means an insecticide and/or a fungicide;

"pesticidally active" means having some capacity to kill or repel one or more pests;

"essential oil" means a volatile material, derived from a portion of a plant or manufactured synthetically, often containing a large amount of terpenes;

"neem oil" means the essential oil of, or any substance extracted from, the neem tree and/or from its components (e.g., bark, seeds, roots, leaves, etc.),

"effective amount" means a quantity that provides the desired effect against the pest(s) of concern,

"disposed on," with respect to the location of a pesticide in relation to the packaging material of a composite article, means coated on or applied to such that it is in intimate contact with at least one primary surface of the packaging material;

"incorporated in," with respect to the location of a pesticide in relation to the packaging material of a composite article, means disposed throughout the material (e.g., as where the material has been soaked in a mixture containing the pesticide) or in one or more discreet layers of the material (e.g., as where the material is in the form of a multilayer film in which one or more of the layers is made from a blend including the pesticide),

"flexible" means capable of deformation without catastrophic failure;

"thermoformed" means the use of heat and pressure to create a desired shape;

"substantially rigid" means exhibiting a tendency to maintain a desired shape, even when subjected to a deforming source,

"tray" means a substantially rigid, base portion of a multi-part container.

"foam" means a cellular plastic,

"polymer" means the polymerization product of one or more monomers and is inclusive of homopolymers, copolymers, and interpolymers as well as blends and modifications thereof,

"mer unit" means that portion of a polymer derived from a single reactant molecule, for example, a mer unit from ethylene has the general formula $-CH_2CH_2-$.

"homopolymer" means a polymer consisting essentially of a single type of repeating mer unit;

"copolymer" means a polymer that includes mer units derived from two reactants (normally monomers) and is inclusive of random, block, segmented, graft, etc., copolymers, "interpolymer" means a polymer that includes mer units derived from at least two reactants (normally monomers) and is inclusive of copolymers, terpolymers, tetrapolymers, and the like,

"polyolefin" means a polymer in which some mer units are derived from an olefinic monomer which can be linear, branched, cyclic, aliphatic, aromatic, substituted, or unsubstituted (e.g., olefin homopolymers, interpolymers of two or more olefins, copolymers of an olefin and a non-olefinic comonomer such as a vinyl monomer, and the like);

"(meth)acrylic acid" means acrylic acid and/or methacrylic acid;

"anhydride functionality" means any group containing an anhydride functionality, such as that derived from maleic acid, fumaric acid, etc., whether blended with one or more polymers, grafted onto a polymer, or copolymerized with a polymer,

"anhydride-modified polymer" means one or more of the following: (1) a polymer obtained by copolymerizing an anhydride-containing unsaturated monomer with a comonomer, (2) an anhydride-grafted copolymer, and (3) a mixture of a polymer and an anhydride-containing compound,

"longitudinal direction" means that direction along the length of a film, i.e., in the direction of the film as it is formed during extrusion and/or coating,

"transverse direction" means that direction across the film and perpendicular to the machine direction;

"free shrink" means the percent dimensional change, as measured by ASTM D 2732, in a 10 cm × 10 cm specimen of film when it is subjected to heat,

as a verb, "laminate" means to affix or adhere (by means of, for example, adhesive bonding, pressure bonding, corona lamination, and the like) two or more separately made film articles to one another so as to form a multilayer structure, as a noun, "laminate" means a product produced by the affixing or adhering just described.

"directly adhered," as applied to film layers, means adhesion of the subject film layer to the object film layer, without a tie layer, adhesive, or other layer therebetween

"between," as applied to film layers, means that the subject layer is disposed in the midst of two object layers, regardless of whether the subject layer is directly adhered to the object layers or whether the subject layer is separated from the object layers by one or more additional layers.

"inner layer" or "internal layer" means a layer of a film having each of its principal surfaces directly adhered to one other layer of the film;

"outer layer" means a layer of a film having less than both of its principal surfaces directly adhered to other layers of the film.

"inside layer" means the outer layer of a film in which a product is packaged that is closest, relative to the other layers of the film, to the packaged product;

"outside layer" means the outer layer of a film in which a product is packaged that is farthest, relative to the other layers of the film, from the packaged product;

"barrier layer" means a film layer capable of excluding one or more gases (e.g., O_2).

"abuse layer" means an outer layer and/or an inner layer that resists abrasion, puncture, and other potential causes of reduction of package integrity and/or appearance quality;

"tie layer" means an inner layer having the primary purpose of providing interlayer adhesion to adjacent layers that include otherwise non-adhering polymers;

"bulk layer" means any layer which has the purpose of increasing the abuse resistance, toughness, modulus, etc., of a multilayer film and generally comprises polymers that are inexpensive relative to other polymers in the film which provide some specific purpose unrelated to abuse resistance, modulus, etc., and

"seal layer" (or "sealing layer" or "heat seal layer" or "sealant layer") means

(a) with respect to lap-type seals, one or more outer film layer(s) (in general, up to the outer 75 μm of a film can be involved in the sealing of the film to itself or another layer) involved in the sealing of the film to itself, another film layer of the same or another film, and/or another article which is not a film, or

(b) with respect to fin-type seals, an inside film layer of a package, as well as supporting layers within 75 μm of the inside surface of the innermost layer, involved in the sealing of the film to itself;

as a noun, "seal" means a bond of a first region of a film surface to a second region of a film surface (or opposing film surfaces) created by heating (e.g., by means of a heated bar, hot air, infrared radiation, ultrasonic sealing, etc.) the regions (or surfaces) to at least their respective softening points so as to cause bonding between polymer chains

The composite article of the present invention can be used to package a variety of goods and can provide protection against many types of fungi and insects. Because of the somewhat unique characteristics of essential oils, especially neem oil, the composite article of the present invention can be tailored to exhibit repellent, biocidal, and/or anti-feedant characteristics. Beneficially, essential oils such as neem oil (or one or more of the components thereof) can be incorporated into packaging materials without changing the performance, feel, odor, appearance, etc., of those materials. Also, the sensory characteristics (e.g., feel, taste, appearance, etc.) of a product packaged in a composite of the present invention do not change substantially, if at all.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

In its broadest sense, the composite article of the present invention involves the use of a particular class of pesticides in combination with a packaging material. The class of pesticides in question includes essential oils (particularly neem oil), those components of the oil that have pesticidal activity, and pesticides such as DEET.

As mentioned previously, the neem tree is a tropical, seed-bearing evergreen. Like extracts of many other plants, extracts of the neem seed are known to influence the feeding behavior, metamorphosis, fecundity, and fitness of numerous species from various orders of insects. This is particularly true of those extracts containing one or more liminoids and/or trithiolane. (Liminoids as a group make up no more than about 6% of neem oil.) Examples of useful liminoids include but are not limited to azadirachtin, salannin, limbindiol, limbin, 6-acetyl limbindiol, deacetyl nimbin, and deacetyl salannin. Particularly preferred liminoids include azadirachtin and salannin.

A number of patents assigned to Thermo Trilogy Corp. of Waltham, Massachusetts (e.g., U.S. Patent Nos. 5,626,848 (Barnette et al.), 5,409,708 (Locke et al.), and 5,356,628 (Locke et al.), the teachings of which are incorporated herein by reference), give excellent, detailed summations of neem oil, its components, and their use as pesticides. Nevertheless, a brief summary is included here for the convenience of the reader.

Neem seeds can be pressed or extracted (e.g., with alcohol) so as to provide neem oil and azadirachtin, respectively. Hand kneading neem seed powder after the addition of water can produce small amounts of neem oil. The previously incorporated U.S. Patent No. 5,356,628 teaches the hydrophobic solvent extraction of ground neem seeds. Useful hydrophobic solvents include aliphatic hydrocarbons, halogenated aliphatic hydrocarbons, petroleum distillates, petroleum ethers, and substituted and unsubstituted aromatic compounds. Alternatively, U.S. Patent No. 5,397,571 (Roland et al.), the disclosure of which is incorporated herein by reference, teaches simultaneous extraction of the hydrophilic and hydrophobic extracts of neem seeds using a mixture of a non-polar, aliphatic hydrocarbon solvent (such as those just listed) and a polar solvent (e.g., an alcohol or ketone).

Thus, the term "neem oil" encompasses a wide variety of materials that can be removed by physical or chemical means from the neem seed, i.e., extractable materials. These extractable materials contain a mixture of hydrophilic and hydrophobic materials, and that mixture varies depending on the extraction technique used. This variety of extraction methods and the resulting compositions of extracted materials has led to some confusion as to the true properties of neem oil. For example, some studies have reported that neem oil shows no or little activity against a variety of insects and/or fungi whereas others have reported substantial pesticidal activity of several species of fungi and/or insects. However, the improved extraction techniques described above have yielded very active neem oil/components of neem oil.

Although crude neem oil does not possess good shelf stability (i.e., loses pesticidal activity over time), those components that inhibit stability can be removed by solvent extraction or by reaction, as taught in the previously incorporated U.S. Patent Nos. 5,409,708 and 5,626,848, respectively. In brief summary, the former patent teaches fractionation of the non-polar hydrophobic solvent extract of neem oil so as to separate the waxes contained therein from the oil; the latter patent teaches reaction of the non-polar hydrophobic solvent extract of neem oil with an aqueous base (to precipitate the waxy components) or a lipid-degrading enzyme. The resulting clarified oil, although essentially free of azadirachtin, demonstrates potent pesticidal activity (e.g., an ability to repel and kill insects as well as an ability to kill insect eggs and larvae) while exhibiting very low phytotoxicity. The wax fraction demonstrates a superior ability to kill insect eggs but exhibits relatively high phytotoxicity.

As can be seen from this brief summary, the neem seed contains numerous components that, both together and individually, can act as pesticides. A non-limiting list of pesticidally active components include azadirachtin, salannin, limbindiol, limbin, 6-acetyl limbindiol, deacetyl nimbin, deacetyl salannin, and trithiolane. Some of these components (e.g., trithiolane) have relatively high vapor pressures (i.e., are relatively volatile) whereas others (e.g., the liminoids) have relatively low vapor pressures (i.e., are relatively non-volatile). Among those components that are preferred for some applications are azadirachtin, salannin, and trithiolane.

In addition to neem oil, other essential oils or the pesticidally active component(s) thereof can be used as the pesticide in the composite article of the present invention. Non-limiting examples of potentially useful essential oils include, for example, the aforedescribed neem oil, lemon oil, thyme oil, geranium oil, citronella oil, balsam oil, sagebrush oil, various mint oils, bergamot oil, chrysanthemum oil, and the like. Preferred amount the foregoing are neem oil and thyme oil. In tests involving some of the most commonly troublesome insects, neem oil and thyme oil have shown the greatest repellency; however, other essential oils are expected to be active against other insects and/or fungi.

As an alternative, or in addition to the essential oils, other pesticidally repellent materials can be used as the pesticide in the composite article of the present invention. An example of such materials is the aforementioned DEET. Because many such materials are not approved for food contact, they preferably are incorporated into or on secondary packaging materials such as, for example, shrink wrap-type thermoplastic film.

The composite article of the present invention involves a packaging material with an effective amount of one of the just-described pesticides disposed on or incorporated in the packaging material. The types of packaging materials that can be used in the present invention are numerous and varied. For ease of description, the following discussion will be divided into the manner in which the pesticide(s) is/are applied to the packaging material.

First, the pesticide can be applied to a surface of the packaging material. Such surface application likely finds greatest utility with non-thermoplastic packaging materials such as, for example, cellophane, paper and/or paperboard (e.g., chipboard and cardboard), although thermoplastic materials can be prepared in a similar fashion. Where the pesticidally active material(s) is a liquid, it can be applied to the packaging material neat; alternatively, regardless of whether or not it is a liquid, it can be dissolved or dispersed in a carrier material (e.g., a solvent or paste) which is then applied to the packaging material. Application to the packaging material can be by one of many well known techniques such as solvent (or dispersant) coating, gravure coating, knife coating, and the like. Such coatings can be as thick or thin as is practical for the particular end use application.

Coated paper and/or cellophane can be used to wrap a variety of products such as, for example, candy, spices, drink mixes, snack foods, and the like. Coated paperboard can be used in the packaging of, for example, processed and unprocessed grains, raisins, chocolate, pasta, and the like. Although some pesticidally active components of various essential oils, including neem oil, likely can contact food products safely, the food-contact side of the packaging material is likely to be the side of the packaging material opposite the coated side. In this type of arrangement, both relatively volatile and non-volatile components can find utility in repelling and/or killing insects.

Alternatively, the pesticide can be disposed within the packaging material. In this embodiment, the packaging material can be non-thermoplastic, such as those materials described in the preceding paragraphs, or thermoplastic. Each is discussed separately below.

Non-thermoplastic materials such as paper and paperboard can be impregnated with pesticide either during or after production. With respect to the former option, the pesticide component(s) can be included in the slurry from which the packaging material is made; with respect to the latter, the already formed packaging material can be dip coated in a solution containing the pesticidal component(s). Either way, the pesticide ends up entrapped in or coated on the fibers of the packaging material and is dispersed relatively evenly throughout the cross section of the packaging material. In this case, if one wishes to ensure that the pesticide(s) do not come into contact with the packaged product, a secondary packaging material can be used to separate the pesticide-containing packaging material from the product.

Thermoplastic materials advantageously can be prepared from resin blends that contain an essential oil or one or more of its aforementioned pesticidally active components. Depending on the types of resin(s) used and the processing conditions, the resulting article can be substantially rigid (e.g., a tray) or can be flexible (e.g., a film).

With respect to articles that are substantially rigid, such articles can be pressed from relatively thick films (e.g., those with a thickness greater than about 150 or about 200 μm) such as, for example, polyvinyl chloride (PVC), polyesters such as polyethylene terephthalate (PET), high density polyethylene, and polystyrene; can be made from a foam such as, for example, those made from epoxy, urethane, phenolic, or styrenic materials; or can be formed from, for example, cellulose pulp, paperboard, and the like. Blending the desired pesticide(s) directly into the mixture from which the foam is formed can result in a composite article of the present invention in the form of a tray. Trays often are used in the packaging of oxygen- and/or moisture-sensitive products; specifically, a product is placed in a preformed tray which is then sealed with a thermoplastic film that inhibits the transmission therethrough of the compound to be excluded (e.g., O_2 and/or H_2O). Examples of such thermoplastic films are those containing one or more layers of nylon, ethylene/vinyl alcohol copolymer (EVOH), poly(vinylidene chloride), and the like. (Of course, in the structure just described, the pesticide can be located in the covering film as well as or instead of in the tray.)

With respect to flexible articles (e.g., films), a monolayer film can be prepared from a blend of a desired resin (or blend of resins) and as little as about 1×10^{-8} percent, preferably as little as about 1×10^{-6} percent, more preferably as little as about 0.00001%, even more preferably as little as about 0.0001 percent, still more preferably as little as about 0.001 percent, yet still more preferably as little as about 0.01 percent, and most preferably as little as about 0.1 percent (all of the foregoing percentages are by weight), of the desired pesticide. Alternatively, a multilayer film structure in which one or more of the layers contains an effective amount of a pesticide including an essential oil or at least one pesticidally active component thereof can provide the desired protection.

Where a film having one or more pesticidally active layers is desired, an essential oil or its pesticidally active component(s) can be included in the resin blend from which the pesticidally active layer(s) are made and the multilayer film prepared according to standard film making techniques known in the art. Alternatively, neat pesticide or a mixture of pesticide in a carrier (e.g., a solvent, paste, etc.) can be applied to the surface(s) of one or more layers of a film. Other layers or separately prepared films can be laminated to the coated film if so desired.

The particular manufacturing process chosen depends strongly on the ultimate end use for the article. Specifically, where an oriented film is desired, the film can be made by a technique that biaxially orients the film during the manufacturing process (e.g., a single- or double-bubble process), where a heat set film is desired, a pre-made film can be heat annealed, where a non-shrink multilayer film is desired, lamination or coextrusion techniques can be employed; etc. The ordinarily skilled artisan is aware of numerous film making techniques available throughout the industry including, but not limited to, free film extrusion, extrusion coating, film casting, coextrusion, and the like.

Although monolayer films find utility in certain packaging operations, most packaging applications call for a variety of properties that can be provided more readily by multilayer films. Examples of such properties that can be built into a film include, for example, orientability, oxygen or moisture barrier, oxygen permeability, free shrink, shrink tension, gloss, low haze, transparency, low or high modulus, high seal strength, differential sealability (between opposing outer layers), and the like. The ordinarily skilled artisan is aware of the types of layers that can provide a given characteristic and, given a combination of characteristics to be included in a given film, can envision numerous film structures that can provide such a combination.

Depending on the desired end use application, the pesticide can be incorporated in an inner layer or an outer layer of the film. For example, one desiring across-the-board protection might wish to blend the desired pesticide into one or more layers of a film. Where one wishes to immediately repel insects from a packaged product, one can incorporate a relatively volatile component into an outer layer of a film. Where one wishes to repel insects from a packaged product over an extended period of time, one can incorporate a relatively volatile component into an inner layer of a film and allow the component to migrate or exude to the surface over time. Where one is not concerned about repellency but wishes to keep an insect from chewing on the composite article, one can incorporate a component which displays anti-feedancy properties into an outer layer of a film. Where a combination of properties is desired, various components can be blended into one or more layers of the film. Based on the foregoing, the ordinarily skilled artisan can envision numerous combinations of film layers and components. Each such combination is within the scope of the present invention.

Where the composite article of the present invention is a film, it can have any total thickness as long as it provides the desired properties for the particular application for which it is to be used. Generally, films to be used as sheeting have thicknesses of at least about 250 μm whereas films used in packaging operations have total thicknesses of less than about 250 μm, preferably from about 5 to about 200 μm, more preferably from about 7.5 to about 150 μm, and yet still more preferably from about 10 to about 125 μm.

The composite article of the present invention encompasses films of both the shrink and non-shrink varieties. For purposes of the present invention, shrink films are those which have a total free shrink of at least about 5%, preferably at least about 10%, and more preferably at least about 20%. Non-shrink films have a total free shrink of no more than about 5%, preferably no more than about 3%, and more preferably no more than about 2%.

A film according to the present invention can be oriented, more preferably biaxially oriented. For certain end use applications, the film preferably is both biaxially oriented and heat shrinkable. A film that is oriented has been elongated, commonly at an elevated temperature (i.e., the orientation temperature), then set or locked in the elongated configuration by cooling. This combination of elongation at elevated temperature followed by cooling causes an alignment of the polymer chains to a more parallel configuration, thereby dramatically altering the mechanical properties of the film. When an unrestrained, unannealed, oriented film subsequently is heated to its orientation temperature, the film shrinks almost to its original, i.e., pre-elongation, dimensions. Such a film is said to be heat shrinkable.

Often, the term orientation ratio (i.e., the product of the extent to which a film is oriented in several directions, usually two directions perpendicular to one another) is used when describing the degree of orientation of a given film. Orientation in the machine direction is referred to as drawing, whereas orientation in the transverse direction is referred to as stretching. For films extruded through an annular die, stretching occurs when the film is blown to produce a bubble. Thereafter, drawing occurs when the film passes through two sets of powered nip rolls, with the downstream set having a higher surface speed than the upstream set. The resulting draw ratio is the surface speed of the downstream set of nip rolls divided by the surface speed of the upstream set of nip rolls.

Where the composite article of the present invention is a multilayer film, it can include those films that have one or more of the following types of layers: abuse layers, barrier layers, tie layers, bulk layers, and seal layers. The physical properties required of a film for any given end use application often determine the composition of the film and/or the compositions of the various layers of the film. Where a variety of properties are required, a variety of layers containing differing polymeric components can be, and usually are, employed. For example, where gas barrier properties are desired, a layer including, for example, EVOH, vinylidene chloride copolymer, or one or more of certain polyamides (e.g., nylons) can be included in the multilayer film structure. If the barrier employed is one which is known to be sensitive to moisture, such as EVOH, and the application requires exposure of the film to moisture, then one or more moisture barrier layers also can be included. If the film is likely to be subjected to abuse during handling and/or transport, an abuse layer can be provided (either as an inner or outer layer). One or two seal layers can be provided to allow for sealing of the film to itself or another packaging article during the formation of a package. One or more inner layers also can be provided, and films with at least one inner layer are preferred for many applications.

Where a barrier layer is included, the film can be used in applications in which the product(s) being packaged preferably is to be protected from one or more detrimental materials (e.g., atmospheric O_2). More particularly, the material of the present invention can take the form of stretch film, film suitable for vertical or horizontal form-fill-and-seal end use, lidstock film, film suitable for vacuum skin packaging, film suitable for use as a barrier bag, film suitable for use as a patch bag, film suitable for use in case ready packaging, film suitable for use in a thermoformed container (particularly in a film used as a liner in a thermoformed tray, such as a polystyrene tray), aroma/odor barrier film, film suitable for use in cook-in end use applications (especially heat shrinkable bags, heat shrinkable and non-heat shrinkable casings, and containers thermoformed from non-heat shrinkable films and sheets), and medical film. Those of ordinary skill in the art can envision other packaging applications in which the film of the present invention can be used; these too are within the scope of the present invention.

Where the composite article of the present invention is a multilayer film, those films containing at least one layer including a polymer that includes mer units derived from ethylene can be preferred for some end use applications. These polymers can be ethylene homopolymers or they can also include mer units derived from one or more of (meth)acrylic acid, a C_3-C_{20} α-olefin, (particularly a C_4-C_{10} α-olefin) C_1-C_{20} esters of (meth)acrylic acid, vinyl acetate, and vinyl alcohol. Ionomers also can be useful. Particularly preferred for many applications are ethylene/α-olefin copolymers.

The relatively recent advent of single site-type catalysts (e.g., metallocenes) necessitates further definitional clarification when discussing ethylene homo- and copolymers. Heterogeneous polymers are those having relatively wide variation in molecular weight and composition distribution. Polymers prepared with, for example, conventional Ziegler Natta catalysts are heterogeneous. Such polymers can be used in a variety of layers including the seal layer.

On the other hand, homogeneous polymers have relatively narrow molecular weight and composition distribution. Homogeneous polymers differ structurally from heterogeneous polymers in that they exhibit a relatively even sequencing of comonomers within a chain, a mirroring of sequence distribution in all chains, and a similarity of chain lengths, i.e., a narrower molecular weight distribution. Homogeneous polymers typically are prepared using metallocene or other single site-type catalysts. Homogeneous polymers also can be used in a variety of layers including the seal layer.

The term "ethylene/α-olefin copolymer" as used herein refers both to heterogeneous materials such as low density polyethylene (LDPE), medium density polyethylene (MDPE), linear low density polyethylene (LLDPE), and very low and ultra low density polyethylene (VLDPE and ULDPE), as well as to homogeneous materials which, in general, are prepared by the copolymerization of ethylene and one or more α-olefins. Preferably, the comonomer is a C_4-C_{20} α-olefin, more preferably, a C_4-C_{12} α-olefin, still more preferably, a C_4-C_8 α-olefin. Particularly preferred α-olefins include 1-butene, 1-hexene, 1-octene, and mixtures thereof. In general, from about 80 to 99 weight percent ethylene and from 1 to 20 weight percent α-olefin, preferably from about 85 to 95 weight percent ethylene and from 5 to 15 weight percent α-olefin, a copolymerized in the presence of a single site catalyst. Examples of commercially available homogeneous materials include the metallocene catalyzed Exact™ resins (Exxon Chemical Co., Baytown, Texas), substantially linear Affinity™ and Engage™ resins (Dow Chemical Co., Midland, Michigan), and Tafmer™ linear resins (Mitsui Petrochemical Corp., Tokyo, Japan).

Homogeneous ethylene/α-olefin copolymers can be characterized by one or more methods known to those of skill in the art, such as molecular weight distribution (M_w/M_n), composition distribution breadth index (CDBI), narrow melting point range, and single melt point behavior. The molecular weight distribution, also known as polydispersity, can be determined by, for example, gel permeation chromatography. Homogeneous ethylene/α-olefin copolymers to be used in a layer of the film of the present invention preferably have an M_w/M_n of less than 2.7; more preferably from about 1.9 to 2.5; still more preferably, from about 1.9 to 2.3.

The CDBI of homogeneous ethylene/α-olefin copolymers generally is greater than about 70 percent. CDBI is defined as the weight percent of copolymer molecules having a comonomer content within 50% (i.e., ± 50%) of the median total molar comonomer content. CDBI can be determined by temperature rising elution fractionation as described by, for example, Wild et. al., *J. Poly. Sci. - Poly. Phys. Ed.*, vol. 20, 441 (1982). Linear polyethylene, which does not contain a comonomer, is defined to have a CDBI of 100%. CDBI determination clearly distinguishes homogeneous copolymers (CDBI values generally above 70%) from presently available VLDPEs (CDBI values generally less than 55%).

Homogeneous ethylene/α-olefin copolymers also typically exhibit an essentially single melting point with a peak melting point (T_m), as determined by differential scanning calorimetry (DSC), of from about 60° to 105°C, more precisely a peak T_m of from about 80° to 100°C. As used herein, the phrase "essentially single melting point" means that at least about 80% (by weight) of the material corresponds to a single T_m at a temperature within the range of from about 60° to about 105°C, and essentially no substantial fraction of the material has a peak melting point in excess of about 115°C as determined by DSC analysis (e.g., on a Perkin Elmer™ System 7 Thermal Analysis System). The presence of higher melting peaks has been found to be detrimental to film properties such as haze and seal initiation temperature.

Of course, additives commonly included in thermoplastic films also can be included in a pesticidally active film according to the present invention. Typical additives include antislip agents, antiblocking agents (particularly alkali aluminosilicate ceramic microspheres), antifogging agents, and the like.

The composite article of the present invention encompasses films made by blowing coextrusion, lamination, and casting techniques, as well as other film-forming techniques known in the art. Although this invention is not intended to be limited to a particular type or class of film structure, the types of film structures in which one or more layers might include a pesticidally active component such as those described above include, but are not limited to, relatively simple films such as one-, two-, and three-layer films that include one or more layers including polypropylene (including oriented and biaxially oriented polypropylene), polyethylene (including blown polyethylene), PVC, PET, and the like, as well as the following:

(a) films used to produce bags such as those described in, for example, U.S. Patent Nos. 3,741,253 (Brax et al.), 3,891,008 (D'Entremont), 4,048,428 (Baird), and 4,284,458 (Schirmer),

(b) films used to produce bags for cook-in applications, such as those described in, for example, U.S. Patent Nos. 4,064,296 (Bornstein et al.) and 4,855,183 (Oberle),

(c) films used in connection with patch bags, such as those described in, for example, U.S. Patent No. 4,755,403 (Ferguson),

(d) shrink films such as those described in, for example, U.S. Patent Nos. 4,551,380 and 4,643,943 (both to Schoenberg),

(e) films having oxygen, moisture, or odor barrier functionality such as those described in, for example, U.S. Patent Nos. 4,064,296 (Bornstein et al.), 4,724,185 (Shah), 4,839,235 (Shah), and 5,004,647 (Shah),

(f) films suitable for medical applications such as, for example, those described in U.S. Patent No. 5,695,840 (both to Mueller),

(g) films suitable for use in a thermoformed package such as, for example, those disclosed in U.S. Patent No. 4,735,855 (Wofford et al.),

(h) stretch/shrink-type films such as those disclosed in, for example, U.S. Patent No. 4,617,241 (Mueller)

(i) films suitable for the packaging of flowable or pumpable products such as those disclosed in, for example, U.S. Patent No. 4,746,562 (Fant),

(j) films suitable for packaging, water cooking, and storing food products such as are disclosed in, for example, U.S. Patent Nos. 4,104,404 (Bieler et al.);

(k) hot blown films of a type useful in chub packaging such as are described in, for example, U.S. Patent No. 4,937,112 (Schirmer);

(l) films having LLDPE or LMDPE in a core and/or an intermediate layer, such as those described in, for example, U.S. Patent Nos. 4,532,189 (Mueller) 4,194,039 (Mueller), 4,390,385 (Ferguson et al.), 4,274,900 (Mueller et al.), 4,188,443 (Mueller et al.), and 5,298,302 (Boice),

(m) films having a low shrink energy such as those disclosed in, for example, U.S. Patent Nos. 4,833,024 (Mueller) and 5,023,143 (Nelson),

(n) films suitable for use in vacuum skin packaging applications, such as those disclosed in, for example, U.S. Patent Nos. 4,886,690 (Davis et al.), 4,963,427 (Botto et al.), and 5,075,143 (Bekele),

(o) films including one or more layers that contain a homogeneous polymer such as those disclosed in, for example, European Publication No. 0 597 502 A3 (Babrowicz et al.) as well as U.S. Patent Nos. 5,604,043 (Ahlgren) and 5,491,019 (Kuo), and

(p) films having high oxygen transmission rates such as, for example, those described in U.S. Patent Nos. 5,491,019 (Kuo) and 5,523,136 (Fischer et al.) as well as U.S. Patent Application No. 08/889,000 (Mossbrook et al)

The teachings of each of the foregoing references are incorporated herein by reference.

Where a film according to the present invention includes more than one layer, it preferably includes from 3 to about 20 layers, although any number of layers are feasible as long as the film provides the desired properties for the particular packaging operation in which it is to be used.

The particular layer(s) of the film containing the pesticide and the particular amount of pesticide used depends, of course, on a variety of factors including, but not limited to: the amount and type of pest(s) in question, the duration for which the composite article is to provide protection to the packaged product, the type of pesticidal activity desired (i.e., whether the pesticide is to act as a repellent, an anti-feedant, a biocide, etc.), and the like. As a general guideline, pesticide can be present in the composite article of the present invention in an amount as little as about 1×10^{-8} percent, preferably at least about 1×10^{-6} percent, more preferably at least about 0.00001 percent, even more preferably at least about 0.0001 percent, still more preferably at least about 0.001 percent, yet still more preferably at least about 0.01 percent, and most preferably at least about 0.1 percent (with all of the foregoing percentages being by weight).

Optionally, a film according to the present invention can be subjected to an energetic radiation treatment which induces crosslinking between polymer chains. Examples of energetic radiation sources include, but are not limited to, corona discharge, plasma, flame, ultraviolet, X-ray, γ-ray, β-ray, and high energy electron. Crosslinking of polymeric films by means of irradiation is disclosed in, for example, the previously incorporated U.S. Patent No. 4,064,296 (Bornstein et al.). Suitable levels of radiation range from about 2 to about 15 MR, preferably from about 2 to about 10 MR. As one of ordinary skill in the art can derive from the description of exemplary films *supra*, the precise amount of radiation is dependent on the film composition, thickness, etc., and the desired end use.

The composite article of the present invention can be or can include an irradiated, oriented, heat set film. Additionally, the film of the invention can be laminated, adhesively adhered, extrusion coated, or extrusion laminated onto a substrate to form a laminate.

Objects and advantages of this invention are further illustrated by the following examples. The particular materials and amounts thereof, as well as other conditions and details, recited in these examples should not be used to unduly limit this invention.

EXAMPLES

Examples 1-7

Five 5-layer heat shrinkable films were prepared according to the procedure disclosed in U.S. Patent Nos. 4,551,380 and 4,643,943 (both to Schoenberg), and two 5-layer heat shrinkable films were prepared according to the procedure described in U.S. Patent No. 4,532,189. The only significant deviation from those procedures was that clarified neem oil (Thermo Trilogy Corp.), i.e., the hydrophobic extract of neem seeds, was introduced into an inner and/or an outer layer of the films.

Table 1 describes the composition of the layers in the seven film structures that were made. In this table, "PE 1" is an ethylene/1-octene copolymer with a density of 0.92 g/cc and a 1-octene comonomer content of 6.55% such as, for example, DOWLEX™ 2045.04 LLDPE (Dow Chemical Co.). "Blend 1" includes 75% of two LLDPEs, 15% EVA (with a vinyl acetate content of 3.3%), and 12% of a master batch of 90% EVA and 10% slip and antiblock additives, "Blend 2" includes 83% of two LLDPEs and 17% EVA, and "Blend 3" includes about 90% PD 9302 ethylene-propylene copolymer (Exxon Chemical Co., Houston, Texas), about 10% of PD 4062 E-7 ethylene-propylene copolymer (Exxon Chem. Co.), and 1% slip and antiblock additives.

Table 1

Example No.	Outer-1	Inner-1	Core	Inner-2	Outer-2
1	Blend 1	PE 1	PE 1	PE 1	Blend 1
2	98% Blend 1 + 2% neem oil	PE 1	PE 1	PE 1	Blend 1
3	95% Blend 1 + 5% neem oil	PE 1	PE 1	PE 1	Blend 1
4	95% Blend 1 + 5% neem oil	98 %PE 1 + 2% neem oil	PE 1	98 %PE 1 + 2% neem oil	Blend 1

5	98% Blend 1 + 2% neem oil	95% PE 1 + 5% neem oil	PE 1	95% PE 1 + 5% neem oil	Blend 1
6	98% Blend 2 + 2% neem oil	Blend 3	PE 1	Blend 3	Blend 3
7	95% Blend 2 + 5% neem oil	Blend 3	PE 1	Blend 3	Blend 3

These films were tested against the Indian meal moth, an insect commonly found in grocery stores and food warehouses. The films were formed into sachets, filled with rice, and sealed. A control film having the same structure except no layer included neem oil also was formed into a sachet, filled with rice and sealed. The rice-filled sachets were placed in covered containers and exposed to Indian meal moths. As the containers were covered, no insects escaped therefrom. The insects were supplied with only water during the testing period.

After a few days of exposure, moths had penetrated into sachet made from the control film. However, the sachets made from the films containing neem oil were free of moths. In fact, in those containers, the moths bunched together into a group, did not move much, and were lethargic. Thus, the repellent properties of films containing neem oil in one or more layers was demonstrated.

These films then were tested for their ability to protect shrink-wrapped boxes of commercially available packages of raisins (supplied by Dole Inc.) from damage caused by exposure to the Indian meal moth. Specifically, the films were used to shrink wrap groups of raisin boxes into six-box packages. A pre-wrapped, commercially available package of six boxes of raisins was used as a control.

Indian meal moth worms were placed in a container with each of the six-box packages. The worms were kept away from light and were provided water. After three weeks, the packages were opened to evaluate the damage caused by the worms. Table 2 shows the results.

Table 2

Example No.	Film feeding[1]	Package feeding[2]	Product feeding[3]
Control	100 (A)	100 (A)	50 (A)
1	100 (A)	57 (B)	28 (A)
2	71 (B)	14 (C)	0 (B)
3	57 (B)	14 (C)	0 (B)
4	42 (BC)	0 (C)	0 (B)
5	71 (B)	0 (C)	0 (B)
6	28 (C)	0 (C)	0 (B)
7	0 (D)	0 (C)	0 (B)

1) Percentage of packages showing holes or evidence of insects feeding on film

2) Percentage of packages showing evidence of insects feeding on boxes

3) Percentage of packages containing insects and showing damage to raisins

(Note: Intracolumn numbers followed by the same letter are not statistically different according to Multiple Range Test, P = 0.05.)

The data of Table 2 clearly show that films according to the present invention show superior protection against insect damage compared to presently available commercial packaging film. The amount of damage caused by insects decreases as more neem oil is added to a given film structure.

During the course of the testing several insects escaped from the cardboard box and a few even escaped the plastic tub. This was surprising since the insects had food and water in their boxes and usually try to avoid the light. This clearly showed that the neem oil-containing films had repellent properties.

Example 8

A portion of the film from Example 1 was Mayer bar coated with a neem oil formulation. The formulation included a 1:1 blend of neem oil in VERSAMIDE™ 930 polyamide binder (Henkel Corp., Kankakee, Illinois) that was diluted with n-propyl alcohol (total solid content of 25%).

Example 9

A portion of the film from Example 1 was Mayer bar coated with a neem oil formulation The formulation included a 1 1 blend of neem oil in RD-800 varnish binder (Flint Ink Corp) that was diluted with a volatile solvent

Examples 10-11

The outer surfaces of 1.5 ounce (about 42 5 g) DEL MONTE™ raisin boxes were brush coated with formulations of clarified neem oil in CONTAX™ V acrylic coating (Sun Chemical Co , Northlake, Illinois) The first formulations included 2 g neem oil in 98 g of the binder, and the second formulation included 4 g neem oil in 96 g of the binder

Example 12-13

Empty raisins boxes were soaked for 30-60 minutes in one of two emulsions of neem oil in water and TRYCOL™ 2307 nonyl phenol ethoxylate surfactant (Henkel-EME Corp). The first formulation included 5% (by wt) neem oil, and the other included 1% (by wt) neem oil

Examples 14-43 Tests Conducted by USDA Agricultural Research Service, Grain Marketing and Prod'n Res Unit

In a series of petri dish bottom halves were added food attractant, in the respective petri dish upper halves were placed a predetermined amount of one or more types of insects. Between each pair of petri dish halves was placed a thermoplastic film, some of which were control samples and some of which contained neem oil Each pair of petri dish halves was secured by a rubber band After securing the dish halves, each dish was allowed to sit for approximately 25 days before being examined

Ten dishes were charged with 10 Indian meal moth larvae Five dishes employed standard shrink film (examples 14-18), while five others employed shrink film in which neem oil was incorporated (examples 19-23) Four of the five control samples showed heavy infestation in the lower half (i e , at least 75 larvae) while one control sample showed moderate infestation (i e , less than 50 larvae) In addition, the control samples exhibited large entry/exit holes in the packaging film. In comparison, all five of the treated samples showed only moderate infestation and no obvious entry/exit holes. Further analysis showed that most, if not all, of the infestation of the packages was due to free living Indian meal months in the test chambers. Adult females lai.. eggs on the underside of the films, and the emerging larvae crawled between the underside of the film and the edge of the petri dish bottom half. (As a point of reference, adult female Indian meal moths typically lay in excess of 300 eggs at a time.) Accordingly, films in which neem oil is incorporated show improved resistance to infestation similar to that which occurs at seams and closures in retail packages.

Ten dishes were charged with 10 adult lesser grain borer adult insects. Five of those dishes employed standard shrink film (examples 24-28), while five others employed shrink film in which neem oil was incorporated (examples 29-33).

Dish No	Number of adult insects in bottom half of dish
24	1
25	4
26	0
27	0
28	0
29	0
30	0
31	0
32	0
33	0

Although the lesser grain borer is not a pest which commonly infests retain packages, it is a very good penetrator of packaging materials. Examples 24-33 show that packaging materials according to the present invention show improved resistance to infestation by penetrating insects.

Ten dishes were charged with 10 adult Indian meal moth, 10 lesser grain borer, 10 warehouse beetle, 10 red flour beetle adult insects. Five of the dishes employed standard shrink film (examples 34-38), while five others employed shrink film in which neem oil was incorporated (examples 39-43). Infestation of the dishes was as follows:

Dish No.	Infestation
34	numerous moth larvae, 2 red flour beetles
35	numerous moth larvae, 1 red flour beetle
36	few (≥ 25) moth larvae, 3 warehouse beetles
37	few moth larvae, 3 red-flour beetles
38	few moth larvae, 2 warehouse beetle larva, 1 red-flour beetle
39	numerous moth larvae, 4 red flour beetles, 2 warehouse beetles
40	few moth larvae, 3 red flour beetles, 1 warehouse beetle
41	few moth larvae, 5 red flour beetles, 1 warehouse beetle
42	few moth larvae, 5 red flour beetles, 1 warehouse beetle
43	few moth larvae, 2 warehouse beetle larvae no infestation

These results, especially those involving Indian meal moth larvae, show that films incorporating neem oil are more resistant to infestation than are standard packaging films.

Examples 44-69 Repellency toward beetles

Various solubilized repellents were incorporated into or on a packaging material. Three samples of each structure were made. The samples had the following structures (with all percentages being by weight):

44 -- laminate of two multilayer films, one having an outer nylon abuse layer
45 -- #44 with 5% DEET included in blend from which outer nylon layer derived
46 -- #45 but with another nylon layer extruded over layer including DEET
47 -- #44 with 5% DEET included in blend from which third layer derived
48 -- PVDC-coated nylon laminated to thin polyethylene film
49 -- #48 coated with 5% geranium oil solution
50 -- #48 coated with 10% geranium oil solution
51 -- #48 coated with 15% geranium oil solution
52 -- same as #48
53 -- #52 coated with 5% DEET solution
54 -- #52 coated with 10% DEET solution
55 -- #52 coated with 15% DEET solution
56 -- same as #48

57 -- #56 coated with 5% thyme oil solution
58 -- #56 coated with 10% thyme oil solution
59 -- #56 coated with 15% thyme oil solution
60 -- three-layer shrink film
61 -- #60 with 5.0% neem oil in an outer layer
62 -- #61 with 5.0% additional neem oil in core layer
63 -- cardboard painted with neem oil solution
64 -- filter paper
65 -- #64 sprayed with 21.85% DEET solution
66 -- #64 sprayed with 10% citronella oil solution
67 -- same as #64
68 -- #67 sprayed with 1% neem oil solution
69 -- #67 sprayed with 10% neem oil solution

Each of the above structures was taped onto a piece of cardboard next to a corresponding control structure.

Ten adult insects (saw-toothed or confused flour beetles) were placed onto a Nitex™ screen with a plastic ring (approximately 3 cm in diameter) adhered thereto. (Prior to use, the screen-ring combination was dipped into polytetrafluoroethylene to keep the insects from crawling out.) The screen-ring combination was centered between the test structure and its corresponding control so that the insects were suspended over the two structures.

After about one hour, the number of insects on the respective sides of the ring were counted. This was repeated every hour for an additional five hours. With three repetitions for each samples, this produced a total of 18 data points for each sample. From these data, a subjective insect repellency rating of Poor, Fair, Good, or Excellent was given to each sample. The results are summarized in the table below.

Table 3

Sample number	Saw-toothed beetle Test / Control	Confused flour beetle Test / Control	Subjective Rating
44	47 / 53	60 / 40	--
45	38 / 52	34 / 66	Fair
46	57 / 43	56 / 44	Poor
47	46 / 54	36 / 64	Fair

48	43/57	46/54	--
49	39/61	26/73	Good
50	53/47	30/70	Fair
51	33/67	26/74	Good
52	48/52	52/48	--
53	47/53	41/59	Poor
54	43/57	32/67	Fair
55	46/54	35/65	Fair
56	53/47	53/47	--
57	53/47	42/58	Poor
58	50/50	59/41	Poor
59	39/61	27/73	Good
60	49/51	45/55	--
61	41/59	41/59	Fair
62	58/42	37/63	Poor
63	67/33	21/79	Good
64	--	58/42	--
65	--	06/94	Excellent
66	--	03/97	Excellent
67	--	52/48	--
68	--	37/63	Fair
69	--	18/72	Excellent

The foregoing data show that packaging films according to the present invention generally display repellent characteristics toward the insects tested, and some display excellent repellency.

Examples 70-72. Repellency toward warehouse beetles

Neem oil was incorporated into various films having the following structures (with all percentages being by weight):

70 -- same as #60 above
71 -- same as #62 above
72 -- six-layer film with 5% neem oil included in blend from which outer layer derived

These samples were tested in the same manner as described above with respect to Examples 44-69 with the exceptions that testing was performed in a fish tank and that warehouse beetles were used as the test subject insects. (Because warehouse beetles can fly, a fish tank was used to keep the beetles from escaping) The data from these tests is shown in the table below.

Table 4

Sample number	Test / Control	Subjective Rating
70	5.9 / 4.1	--
71	0.25 / 9.75	Excellent
72	0.17 / 9.83	Excellent

The foregoing data show that packaging films according to the present invention in which neem oil is incorporated into an outer layer display excellent repellent characteristics toward warehouse beetles

Examples 73-76 Anti-Feeding Activity of Neem Oil

A series of packaging films were converted into small bags with dog food snacks hermetically sealed inside (Each film was tested in triplicate, i.e., three separate bags were made from each film.) The bags were placed into fish tanks. The films had the following structures (with all percentages being by weight)

73 -- six-layer coextruded film

74 -- same as #72 above

75 -- #73 with 10% neem oil in one outer and one inner layer

76 -- #73 with 10% neem oil in one outer and one inner layer as well as 5% neem oil in one outer and one inner layer

Ten adult confused flour beetles (CFB) and ten adult warehouse beetles (WB) were placed in each fish tank along with provided foodstuff for three months. After the test period, the packages were evaluated for insect penetration. As before, a subjective insect repellency rating was given to each sample

Table 5

Sample number	Insects penetrating the package	Subjective Rating
73	1 CFB, 1 CFB, 0	--
74	1 CFB+1 WB, 0, 1 CFB	Good
75	0, 0, 0	Excellent
76	0, 1 CFB, 4 CFB	Fair

Because the bag from example 76 contained more neem oil than did the bag from example 75, its poorer performance is surprising and probably anomalous. Nevertheless, the excellent anti-feedency characteristics of example 75 are believed to show the efficacy of neem oil-containing films against penetrating insects such as confused flour beetles and warehouse beetles.

Various modifications and alterations that do not depart from the scope and spirit of this invention will become apparent to those skilled in the art. This invention is not to be unduly limited to the illustrative embodiments set forth herein.

We claim:

1. A composite article comprising

a) a packaging material; and

b) disposed on or incorporated in said packaging material, an effective amount of a pesticide comprising an essential oil or at least one pesticidally active component of an essential oil.

2. The composite article of claim 1 wherein said pesticide is disposed on said packaging material.

3. The composite article of claim 2 wherein said packaging material comprises one or more of paper, paperboard, thermosetting materials, and thermoplastic films.

4. The composite article of any of claims 1 to 3 wherein said pesticide is incorporated in said packaging material.

5. The composite article of claim 4 wherein said packaging material is substantially rigid.

6. The composite article of claim 5 wherein said substantially rigid packaging material is a tray.

7. The composite article of claim 4 wherein said packaging material is flexible.

8. The composite article of claim 7 wherein said flexible packaging material is a thermoplastic film.

9. The composite article of claim 8 wherein said film comprises more than one layer.

10 The composite article of claim 9 wherein at least one of said layers is a barrier layer

11 The composite article of claim 9 wherein an outer layer of said film comprises said pesticide

12 The composite article of claim 9 wherein an inner layer of said film comprises said pesticide

13 The composite article of any of claims 1 to 12 wherein said pesticide comprises neem oil or thyme oil

14 The composite article of any of claims 1 to 12 wherein said pesticide comprises a pesticidally active component of neem oil

15 The composite article of claim 14 wherein said component comprises one or more of azadirachtin, salannin, and trithiolane

16. A package comprising

a) a product; and

b) the composite article of any of claims 1 to 15, wherein said article substantially completely surrounds said product

17 The package of claim 16 wherein said product comprises a food

18 A method of protecting a product from one or more pests comprising substantially completely surrounding said product with the composite article of any of claims 1 to 15 so as to form a package and allowing said composite article to provide protection against said one or more pests

19 The method of claim 18 wherein said one or more pests comprise at least one of fungi and insects

20. A method of making a protective film comprising extruding said film from a mixture comprising at least one resin and a pesticide comprising an essential oil or at least one pesticidally active component of an essential oil

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/17371

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N25/34 A01N65/00 A01N37/18 //(A01N65/00,25:34), (A01N37/18,25:34)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 9406 Derwent Publications Ltd., London, GB; Class A17, AN 94-046624 XP002088393 & RU 2 000 303 C (AS BELO METAL POLYMER SYSTEMS MECH INST), 7 September 1993 see abstract	1,4,7,8, 13,16-20
Y		9-12,14, 15

Y	PATENT ABSTRACTS OF JAPAN vol. 13, no. 562 (C-665), 13 December 1989 & JP 01 233205 A (DAICEL CHEM IND), 19 September 1989 see abstract	14,15

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
17 December 1998	11/01/1999

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No.
Y	H.E.MOLINE ET AL.: "EFFECTS OF NEM SEED OIL ON FIRMNESS AND STORAGE DECAY OF 'GOLDEN DELICIOUS' APPLES" 'ONLINE!, 1 August 1995, XP002088392 Available from Internet: <URL: http://www.nat.usda.gov/ttic/tektran/data/000006/21/00000621196.html> see 'Interpretive Summary'	14,15
Y	GB 1 568 936 A (EXTHENE PTY LTD) 11 June 1980 see page 1, line 23 - line 30 see page 1, line 36 - line 38 see page 2, line 34 - line 37 see page 2, line 41 - line 52	9-11
Y	FR 2 630 088 A (SUMITOMO CHEMICAL CO) 20 October 1989 see page 3, line 7 - line 24	9-11
Y	GB 2 131 740 A (MULTIFOIL PTY LTD) 27 June 1984 see column 2, line 11 - line 14	12
X	EP 0 609 779 A (FUKUNAGA TOSHIKAZU) 10 August 1994 see page 2, line 40 - line 45 see page 3, line 22 - line 28	1-7, 16-19
X	WO 97 06074 A (TIPLER KEITH CHARLES ;TATT IVAN ROBERT (GB)) 20 February 1997 see page 1, paragraph 4 - paragraph 5 see page 1, paragraph 8 see page 2, paragraph 3 see page 2, paragraph 6	1-3,13, 16-18
X	US 4 320 112 A (JONES LONNIE R ET AL) 16 March 1982 see column 1, line 8 - line 13 see column 1, line 62 - line 64 see column 2, line 5 - line 52 see column 3, line 1 - line 23	1,4,5, 7-9, 16-21
A	EP 0 142 658 A (STRAHLEN UMWELTFORSCH GMBH) 29 May 1985 see page 3, line 12 - line 34	1-21

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte onal Application No
PCT/US 98/17371

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
GB 1568936	A	11-06-1980	NONE		
FR 2630088	A	20-10-1989	AU	607321 B	28-02-1991
			AU	3244389 A	19-10-1989
			CA	1303977 A	23-06-1992
			JP	2036109 A	06-02-1990
			US	4966796 A	30-10-1990
GB 2131740	A	27-06-1984	AU	2193483 A	07-06-1984
			FR	2537095 A	08-06-1984
			JP	60034838 A	22-02-1985
			PT	77763 B	10-04-1986
			ZA	8308989 A	25-07-1984
EP 0609779	A	10-08-1994	JP	2566515 B	25-12-1996
			JP	6227931 A	16-08-1994
			AT	171843 T	15-10-1998
			DE	69413725 D	12-11-1998
			US	5468493 A	21-11-1995
WO 9706074	A	20-02-1997	AU	6663696 A	05-03-1997
			CA	2228432 A	20-02-1997
			EP	0842099 A	20-05-1998
US 4320112	A	16-03-1982	NONE		
EP 0142658	A	29-05-1985	DE	3337592 A	25-04-1985
			AU	570077 B	03-03-1988
			AU	3411584 A	18-04-1985
			CA	1263251 A	28-11-1989
			JP	60156330 A	16-08-1985
			US	4743448 A	10-05-1988

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
A01N 25/34, 65/00, 37/18 // (A01N 65/00, 25:34) (A01N 37/18, 25:34)

A1

(11) International Publication Number: **WO 99/09824**

(43) International Publication Date: 4 March 1999 (04.03.99)

(21) International Application Number: PCT/US98/17371

(22) International Filing Date: 19 August 1998 (19.08.98)

(30) Priority Data:
60/056,843 22 August 1997 (22.08.97) US

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(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.
With amended claims

Date of publication of the amended claims: 15 April 1999 (15.04.99)

(54) Title: PESTICIDAL PACKAGING MATERIALS

(57) Abstract

A pesticide is disposed in or on a packaging material to provide a composite article that protects products packaged therein from pest such as fungi and insects. The pesticide includes an essential oil or at least one pesticidally active component of thereof. The packaging material can be flexible or substantially rigid and can be thermoplastic or non–thermoplastic.

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AMENDED CLAIMS

[received by the International Bureau on 3 March 1999 (03.03.99); original claims 1-15 and 20 amended; (3 pages)]

1 A composite article comprising

a) a thermoplastic packaging film, and

b) uniformly distributed in said packaging film or a discreet layer thereof, an effective amount of a pesticide comprising neem oil or at least one pesticidally active component thereof.

2. The composite article of claim 1 wherein said film comprises more tha one layer.

3. The composite article of claim 2 wherein at least one of said layers is an oxygen barrier layer.

4. The composite article of any of claims 1 to 3 wherein said pesticide is uniformly distributed throughout an outer layer of said film.

5. The composite article of any of claims 1 to 3 wherein said pesticide is uniformly distributed throughout an inner layer of said film.

6. The composite article of any of claims 1 to 5 wherein said pesticide comprises a pesticidally active component of neem oil.

7. The composite article of claim 6 wherein said at least one component is free of halogen atoms.

8. The composite article of claim 6 wherein said component comprises one or more of azadirachtin, salannin, and trithiolane.

9 The composite article of any of claims 1 to 8 wherein said pesticide repels insects.

10 The composite article of any of claims 1 to 8 wherein said insecticide kills insects

11 The composite article of any of claims 1 to 10 wherein said thermoplastic packaging film comprises a polymer comprising mer units derived from ethylene

12. The composite article of claim 11 wherein said polymer further comprises mer units derived from at least one of (meth)acrylic acid, a C_3-C_{20} α-olefin, C_1-C_{20} esters of (meth)acrylic acid, vinyl acetate, and vinyl alcohol

13. The composite article of any of claims 1 to 12 wherein said thermoplastic packaging film comprises at least one of an antiblocking agent, a slip agent, and an antifogging agent.

14. The composite article of any of claims 1 to 13 wherein said thermoplastic packaging film is biaxially oriented

15. The composite article of any of claims 1 to 14 wherein said thermoplastic packaging film has a thickness of from 10 to 125 μm

16. A package comprising:

a) a product; and

b) the composite article of any of claims 1 to 15, wherein said article substantially completely surrounds said product.

17. The package of claim 16 wherein said product comprises a food

18 A method of protecting a product from one or more pests comprising substantially completely surrounding said product with the composite article of any of claims 1 to 15 so as to form a package and allowing said composite article to provide protection against said one or more pests

19. The method of claim 18 wherein said one or more pests comprise at least one of fungi and insects.

20. A method of making a protective film comprising extruding said film from a mixture comprising at least one resin and a pesticide comprising neem oil or at least one pesticidally active component thereof